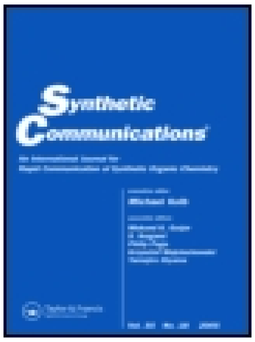

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Fe_3O_4-Graphene oxide nanocomposite: Synthesis of 5-sulfanyl tetrazole derivatives of alkyls, indoles, and pyrroles

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ABSTRACT

In this work, the use of Fe_3O_4/geraphene oxide nanocomposite as an efficient catalyst for the synthesis of 5-sulfanyltetrazole derivatives of indoles, pyrroles, and 5-alkyl sulfanyltetrazoles is described. These compounds are readily obtained by the reaction of the starting heterocycles indoles, N-aryl pyrroles, alkyl thiocyanates, and trimethylsilyl azide in good to excellent yields. Moreover, Fe_3O_4/GO nanocomposite could be easily separated from the reaction mixtures by an external permanent magnet and reused at least six times continuously without significant reduction in the product yield and its catalytic activity.

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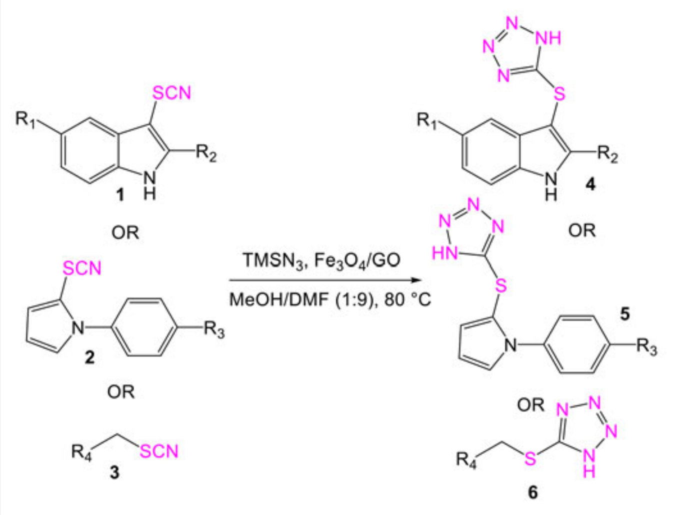
KEYWORDS
Fe_3O_4/geraphene oxide; heterogeneous; indoles; nanocomposite; N-aryl pyrroles; sulfanyltetrazole

GRAPHICAL ABSTRACT



Introduction

Tetrazole as a five-membered aromatic nitrogen-containing ring is an important heterocyclic scaffold and although not found in nature, it has received much attention in both

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chemistry and biology. Also, it can be considered as carboxylic acid isosteres because of greater metabolic stability.[1]

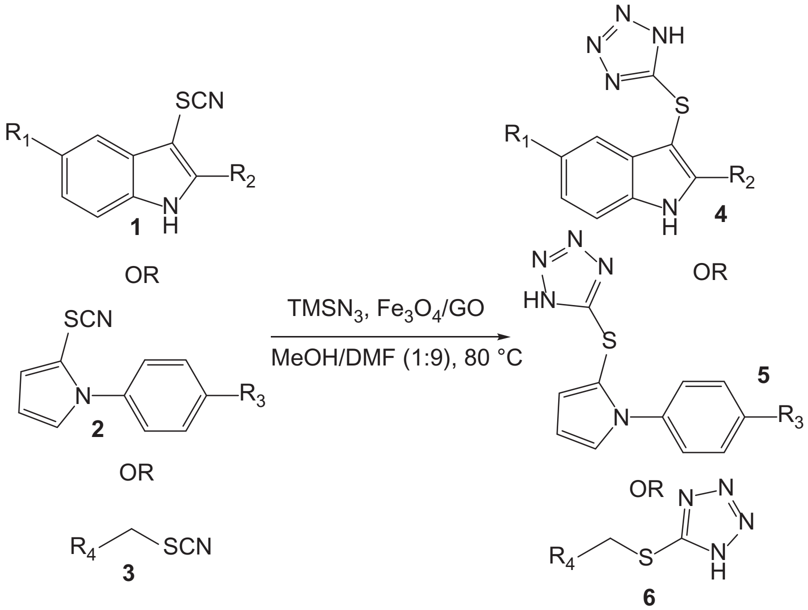
Among the tetrazoles family, 5-substituted tetrazoles have been found to be abundant in active biological compounds.[2] Tetrazole moieties can be used in synthetic organic chemistry,[3] coordination chemistry,[4] energetic materials,[5,6] photography,[7] and agriculture.[8]

Sulfanyltetrazoles as a subunit of tetrazoles are increasingly used in drug combinations as a pharmacophore,[9] with applications such as activator in RNA synthesis,[10] antimycobacterial,[11] antibacterial[12–14] and anti-HIV agents.[15] It has been demonstrated that compounds containing sulfanyltetrazole structures are significant scaffolds with great potential for therapeutic activity.[16]

Considering the many applications and development of tetrazoles to a wide variety of biological agents, there is a big demand for the various methods of synthesizing sulfanyltetrazoles. During recent decades, various and practical methods for the synthesis of tetrazole derivatives have been proposed.[17–21] Due to the lack of publications on the heterogeneous synthesis of sulfanyltetrazoles,[11,22–27] it would be desirable to attend to the preparation of these compounds with heterogeneous catalysts. Herein, in continuation of our studies on the compounds containing sulfanyltetrazole as antibacterial agents[12,13] and focusing on the potential of these materials for a variety of biological applications, we synthesized 5-sulfanyl tetrazole derivatives of alkyls as well as indoles and pyrroles, which are rarely reported.[28,29]

In recent years, magnetic nanoparticles have provided new pathways for the development of recyclable heterogeneous catalysts.[30] In particular, Fe_3O_4/geraphene oxide (GO) nanocomposites have received much attention and have been widely used as nanocatalysts.[31–33]

GO is one of the most important graphene derivatives. It is a good candidate for supporting metal and metal oxide nanoparticles due to the unique planar structure, high chemical stability, large surface area, and variety of oxygen-containing functional groups.[34]



Scheme 1. Sulfanyltetrazoles synthesis ctalayzed by Fe_3O_4@GO nanocomposite

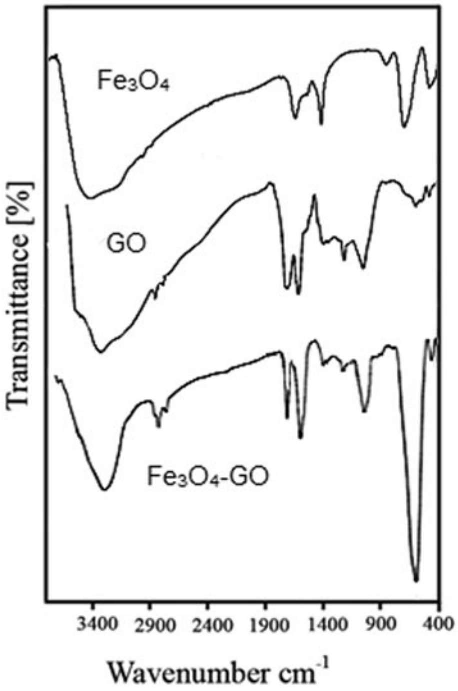


Figure 1. FTIR spectrum of (a) Fe_3O_4, (b) GO, and (c) Fe_3O_4/GO.

In this study, we prepared a magnetically recyclable heterogeneous Fe_3O_4/GO nanocomposite for the synthesis of some 5-sulfanyl tetrazole derivatives including alkyls, indoles, and pyrroles. The catalyst produced the desired products with good yields and could be reused for several cycles with high catalytic activity, which indicates its applicability as a reusable catalyst for the synthesis of sulfanyltetrazole derivatives.

Results and discussion

Chemistry

Synthesis of sulfanyltetrazoles was achieved through the synthetic pathways as presented in Scheme 1. As depicted in Scheme 1, the reaction between thiocyanate derivatives and $TMSN_3$ and Fe_3O_4@GO nanocomposite in DMF/MeOH (9:1) at 80 °C provided related sulfanyltetrazoles. Fe_3O_4@GO nanocomposites were prepared according to a previously reported procedure with some modifications.[31]

The synthesized nanocomposites were characterized by, FT-IR, powder XRD, VSM, TEM and SEM analysis.

Figure 1 shows FT-IR spectra for Fe_3O_4, GO, and Fe_3O_4-GO, in both cases, show bands around 585 cm^{-1}, those bands are associated to the stretching vibration modes of the magnetite Fe–O bonds. There are also present C=O stretching vibrations (1716 cm^{-1}) and O–H stretching vibrations (3375 cm^{-1}). Fe_3O_4-GO spectrum has prominent O–H and C=O signals, due to the functional groups present on the GO sheets.

Figure 2 shows the XRD pattern of GO and magnetite nanocomposite. As shown in the XRD pattern of Fe_3O_4-GO, all the characteristic peaks of nanoparticles and GO

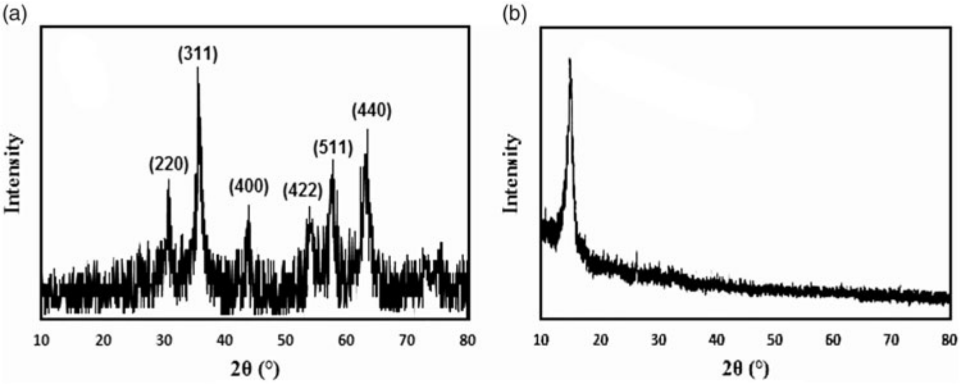


Figure 2. XRD pattern of (a) Fe_3O_4/GO and (b) GO.

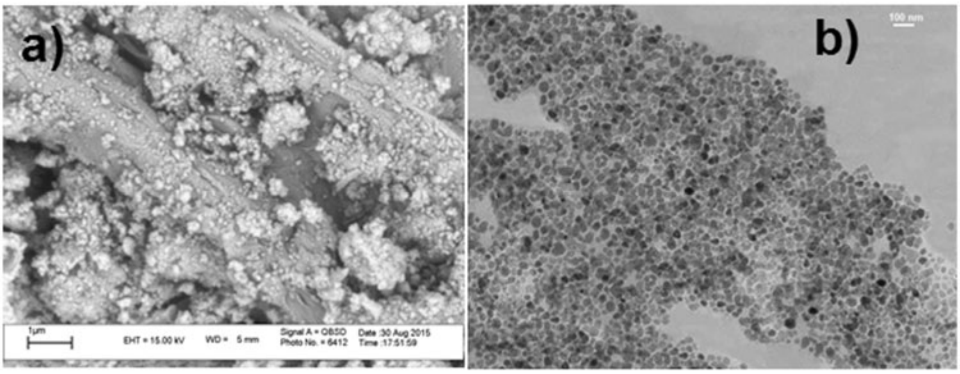


Figure 3. (a) SEM image, (b) and TEM image of Fe_3O_4/GO.

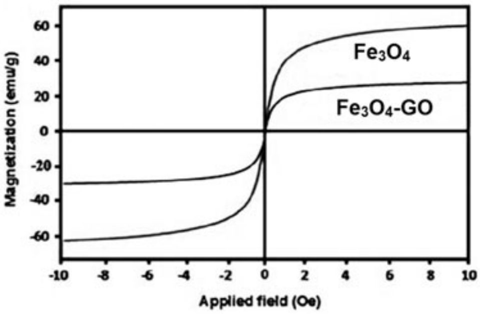


Figure 4. Vibrating-Sample magnetometer (VSM) patterns of $Fe_3O_4$and Fe_3O_4/GO.

were identified in the spectrum of Fe_3O_4-GO nanocomposites. The peaks at 2θ values of 30.2° (200), 35.5° (311), 43.3° (400), 53.7° (422), 57.1° (511), and 62.9° (440) were consistent with the standard XRD data for the magnetite phase (JCPDS no. 19–0629). However, no diffraction peak of GO is observable for the as-prepared Fe_3O_4@GO composite, suggesting that the layer stacking of the GO sheets was destroyed by the loading of Fe_3O_4 NPs. This confirmed that pure phase Fe_3O_4-GO was successfully formed.

Table 1. Optimization of the catalyzed formation of sulfanyltetrazole (4a).

Entry	Catalyst(g)	Solvent	Temperature(°C)	Yield(%)[a]
b	–	DMF/MeOH(9:1)	80	42
2	–	DMF	110	23
3	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	110	77
4	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	90	78
5	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	80	82
6	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	70	67
7	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	60	42
8	Fe_3O_4/GO(0.05)	DMF/MeOH(9:1)	80	90
9	Fe_3O_4/GO(0.03)	DMF/MeOH(9:1)	80	90
10	Fe_3O_4/GO(0.01)	DMF/MeOH(9:1)	80	66
11	Fe_3O_4/GO(0.03)	DMF	80	76
12	Fe_3O_4/GO(0.03)	DMSO	80	Trace
13	Fe_3O_4/GO(0.03)	Toluene	80	0
14	Fe_3O_4/GO(0.03)	THF	80	0
15	Fe_3O_4/GO(0.03)	H_2O	80	0
16	Fe_3O_4/GO(0.03)	NMP	80	0
17	Fe_3O_4/GO(0.03)	Dioxane	80	0
18	Fe_3O_4(0.03)	DMF/MeOH(9:1)	80	52
19	GO(0.03)	DMF/MeOH(9:1)	80	0

[a] Isolated yield.

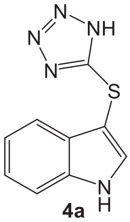
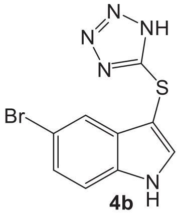
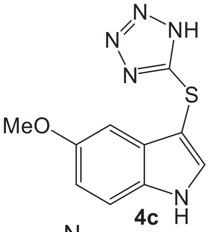
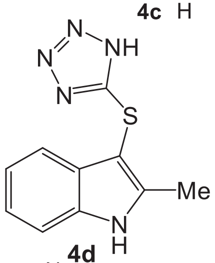
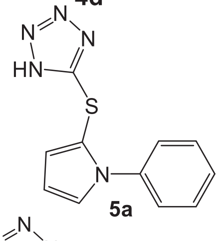
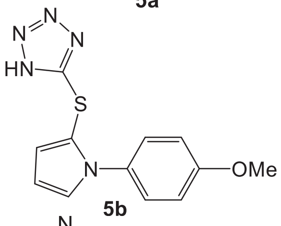
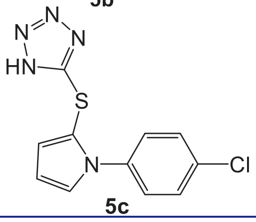
The morphology of the obtained Fe_3O_4-GO nanocomposites was also characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 3, the micrographs of the prepared Fe_3O_4-GO composites revealed that Fe_3O_4 nanoparticles distributed homogeneously in the GO surfaces of the nanocomposites. Also, TEM images proved that the cubic crystal structure and the morphology of Fe_3O_4 NPs on the GO sheets remain unchanged after the recycling.

Next, the magnetic properties of Fe_3O_4-GO nanocomposite were investigated using VSM at room temperature (Figure 4). The Fe_3O_4-GO nanocomposites showed a typical S-like magnetic hysteresis loop with the specific saturation magnetization (Ms) of ~26 emu/g. This value exhibits superparamagnetic behavior. These phenomena were consistent with the results obtained from FT-IR, SEM, TEM, and XRD.

The results of the optimization of reaction conditions are summarized in Table 1. The control reactions showed that In the absence of a catalyst at 80 and 110 °C, no reaction occurred after 24 h (Table 1, entries 1–2). The effect of temperatures on the reaction was investigated. Increasing or decreasing the reaction temperature will not dramatically improve the yield of the reaction (Table 1, entries 3–7). The results on the change of catalyst loadings showed that catalyst loadings of 0.03 g showed better performance than that with catalyst loadings of 0.05 g, which had no effect on the yield of the reaction. Catalyst loading of 0.01 g was not sufficient for the reaction (Table 1, entries 8–10). The Solvent has a decisive influence on the efficiency of the reaction. The experimental results show that DMF is good solvent with 76% yield, whereas DMSO, toluene, THF, H_2O, NMP, and dioxane are not suitable for the reaction (Table 1, entries 11–17). Bare Fe_3O_4 nanoparticles have been provided 52% product conversion after 24 h. (Table 1, entry 18). Only GO showed no catalytic activity for this reaction (Table 1, entry19).

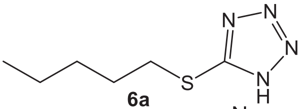
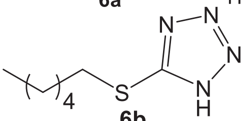
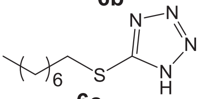
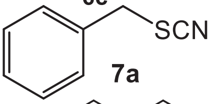
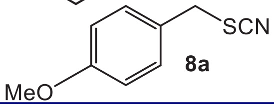
Using the results presented in Table 1, we investigated the scope and limitation of the reaction on a variety of organic thiocyanates. To achieve this goal, a set of 4 Indoles, 3 Pyrroles, and 5 non-aromatic thiocyanate derivatives were subjected to general reaction conditions. Tetrazole derivatives of indoles and pyrroles were synthesized conveniently

Table 2. Fe_3O_4/GO catalyzed synthesis of sulfanyltetrazoles[a].

Entry	Product	Time(h)	Yield(%)[b]
1	 **4a**	3	90
2	 **4b**	4	92
3	 **4c**	4	60
4	 **4d**	5	80
5	 **5a**	3	92
6	 **5b**	3	90
7	 **5c**	3.5	91

(*continued*)

Table 2. Continued.

Entry	Product	Time(h)	Yield(%)[b]
8	 **6a**	6	82
9	 **6b**	6	84
10	 **6c**	8	80
11	 **7a**	24	0
12	 **8a**	24	0

[a]Thiocyanate (1 mmol), $TMSN_3$ (1.5 mmol), F_3O_4/GO (0.03 g), DMF/MeOH(9:1) (5 mL), 80 °C.
[b]Isolated yield.

Table 3. The effect of the mass ratio of Fe_3O_4 to GO on the activity of the catalyst.

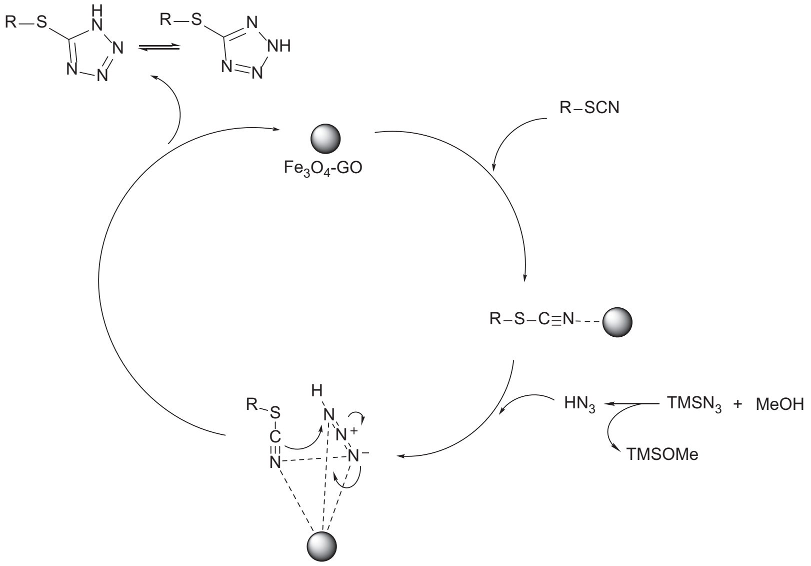
The mass ratio of Fe_3O_4 to GO	Yield of reaction (%)
2	47
5	77
10	90
15	88
20	87

in good to high yields (Table 2, Entries 1–7). With non-aromatic thiocyanates, which have a thiocyanate substituent at the benzylic position, the reactions did not proceed (Table 2, Entries 11 and 12). The reaction of (8–10) gave the corresponding tetrazoles in good to moderate yields, but they need more reaction time to reach completion.

Investigations showed that the Fe_3O_4 to GO mass ratio in Fe_3O_4-GO nanocomposite plays an important role in its catalytic activity. As shown in Table 3, for the reaction of 3-thiocyanato-1H-indole, the reaction efficiency increases with an increase in the mass ratio of Fe_3O_4 to GO of 10. Increasing the amount of Fe_3O_4 does not have a beneficial effect on improving the reaction efficiency.

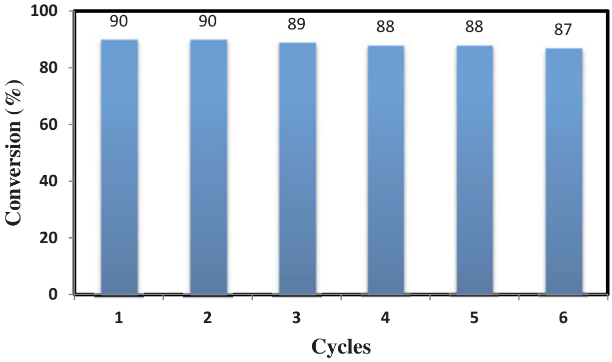
A proposed mechanism for the reaction forming 5-substituted sulfanyl tetrazole in the presence of Fe_3O_4-GO composites as a catalyst is shown in Scheme 2. At the initial stage of the catalytic cycle, the reaction of thiocyanates 1 with catalyst produces the intermediate A; besides, HN_3 B forms *in situ* from the reaction of $TMSN_3$ and MeOH.[9] The [3 + 2] cycloaddition between the triple bond of the intermediate A and HN_3 B takes place readily to form the intermediate C. It seems that the triple bond is activated by forming an A species, which makes the [3 + 2] cycloaddition feasible. Protonolysis of the intermediate C affords the 5-substituted sulfanyl tetrazole 3.

The reusability of the catalyst has been studied. For this purpose, the reaction of 3-thiocyanato-1H-indole was carried out under optimized conditions. After carring out



Scheme 2. Proposed mechanism for the synthesis of sulfanyltetrazoles using Fe$_3$O$_4$/GO.

Table 4. Catalyst reusability study.



the reaction, the catalyst was centrifuged, washed with ethanol and water (2–3 times) and dried in vacuum. The catalyst was reused and found not to lose efficiency even after 6 runs. The results are given in Table 4.

Therefore, Fe$_3$O$_4$-GO shows unique virtues, i.e., not only is the catalytic performance comparable with homogeneous catalysts, but also the separation and reuse of the catalyst is easily achieved.

Experimental

Chemicals were either purchased from Merck or synthesized in our laboratory. Commercial reagents and solvents were used without further purification. The IR spectra were recorded on a Bruker Tensor 270 spectrometer using KBr discs. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT- 400 MHz spectrometer at room temperature with DMSO-d$_6$ and CDCl$_3$ as solvents. Elemental analyses were performed on an

Elementar Vario EL III instrument. X-ray diffraction (XRD) patterns of the samples were recorded on a Siemens diffractometer with Cu-Kα radiation at 35 kV in the scan range of 2θ from 10° to 80°. The surface morphologies of samples were examined by a scanning electron microscope (SEM) (LEO 1430VP) under vacuum at an operating voltage of 35 kV. Dried samples were gold coated by sputtering for 15 S. Transmission electron microscope (TEM) images are recorded by using LEO-906 instrument. The magnetic properties were analyzed using a vibrating sample magnetometer at room temperature (VSM; AGFM, Kashan, Iran).

General procedure for the synthesis of the 5-sulfanyltetrazoles

Fe_3O_4@GO (0.03 g) was added to thiocyanate (alkyl, indole or pyrrole) (1 mmol), trimethylsilyl azide ($TMSN_3$) (1.5 mmol), and DMF/MeOH (9:1) (6 mL) and the mixture was stirred at 80 °C for 6 h. After completion of the reaction (as indicated by TLC), the catalyst was separated by applying an external magnetic field and washed thrice with ethanol and water. Then, the reaction mixture was treated with ethyl acetate and 1 N HCl. The resulting organic layer was separated and dried with anhydrous Na_2SO_4, and concentrated. An aqueous solution of NaOH (0.25N) was added to the residue and the resulting mixture was stirred for 30 min at room temperature. The mixture was washed with ethyl acetate, and then conc. HCl was added to obtain the pH value of the water layer to 1. The aqueous layer was extracted with ethyl acetate (×3) and the combined organic layers were washed with 1 N HCl. The organic layer was dried over anhydrous Na_2SO_4 and concentrated.

Conclusion

In this paper, we reported a simple and practical modification of the sulfanyl tetrazole synthesis route which leads to 5-sulfenyl tetrazole derivatives of indoles, pyrroles, and alkyls directly. A sulfanyltetrazole heterogeneous synthesis using a magnetic catalyst has been developed. Fe_3O_4-GO nanocomposite shows interesting properties, that is, it has the ability to separate and reuse, along with performance comparable to homogeneous catalysts. The chemical efficiency, the low cost of reagents, and the use of environmentally benign catalyst make this process particularly attractive.

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